

New sensing system based on electromagnetic waves and functionalised EM sensors for continuous monitoring of Zn in freshwater

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Abstract

Toxic metals are a significant cause for concern, considering freshwater the major route of their transport even far from point and diffuse sources. This paper presents a novel combined method using electrical measurements and microwave spectroscopy based on functionalised electromagnetic (f-EM) sensors. Thick films based on β - Bi_2O_3 were screen-printed on planar sensors for monitoring continuously Zn concentrations in water. Results demonstrate the capability of this novel sensing system to measure in real-time Zn concentrations, especially in the range 0-1 mg/L and consequently the possibility to detect an unexpected pollution event, which can generate an increase of Zn in water.

Keywords: Zinc, online monitoring, microwave spectroscopy, f-EM sensor, water pollution

Introduction

Metal pollution from both active and abandoned mines is a global environmental problem, with leaching from waste heaps and the groundwater which ascends after pumping stops, being a particular concern (Environment Agency 2008). The combination of point and diffuse sources and freshwater largely determines the dispersion of toxic metals (Cd, Pb, Cu, Zn, Ni, Fe, etc) into the environment. Surface waters are the major dispersion vehicle of pollution of these contaminants.

Zinc (Zn) is an essential element having a role in many biological functions (e.g. cellular metabolism, catalytic activity of enzymes, protein synthesis, and so forth) in living organisms. However, at high concentrations and with long-term exposure, Zn can have toxic effects on humans and other living organisms, that can include respiratory and neuronal disorder (Kashin and Ivanov 2010). Accordingly, several environmental quality standards (EQS) exist for Zn in water; these are summarised in tab. 1 (Edokpayi et al. 2016; UK Technical Advisory Group on

Table 1 Summary of the EQS established for Zinc (in mg/L) by worldwide organisations.

EQS	UK TAG	US EPA	WHO	US EPA	DWAF	DWAF
	UK Technical Advisory Group on the EU Water Framework Directive	US Environmental protection agency	World Health Organisation	US Environmental protection agency	South African Department of Water Affairs and Forestry	South African Department of Water Affairs and Forestry
	Surface water	Surface water	Drinking water	Drinking water	Domestic water use	Protection of aquatic life
Zinc (mg/L)	0.008-0.125 ^a	0.059-0.210 ^a	3	5	3	0.002



the Water Framework Directive 2008). Zn concentrations in mine water typically range from 0.1 to 10 mg/L but can be as high as 500 mg/L (Byrne et al. 2012).

There are many examples where the waste from mining has posed a risk to water resources and to animal and human health. For example, high-flow conditions lead to an increase in Zn concentrations, due to the erosion and weathering of the waste materials and the dissolution of efflorescent salts (Cidu et al. 2011). However, this is not a general rule: at many sites the metal concentrations decrease because of the dilution (Wolkersdorfer 2008). Therefore, proper impact assessment by continuous monitoring of toxic metals in water is essential for the optimal environmental management, understanding better metal dynamics and for planning effective water remediation.

Currently, no method can guarantee in-situ continuous monitoring of water resources. Traditional methods require labour intensive field sampling and costly off-line laboratory-based methods of analysis, limiting the ability to manage remote sites, and the detection of

the immediate effects of accidental contamination events. Consequently, it is necessary to develop advanced sensor technologies for adequate in-situ and real-time water properties monitoring.

Accordingly, a developing sensing system able to monitor Zn ions in mine water continuously is an electromagnetic (EM) wave sensor system, operating at microwave frequencies (Korostynska et al. 2013). This method is able to give an immediate and continuous response at specific frequencies when a water sample with diverse pollutant concentration is placed in vicinity of the EM field. With the purpose to produce a more specific spectral response for measuring a single contaminant at low concentration in water, the synergy with chemical materials is providing interesting advantages (Azmi et al. 2017).

This work reports the preliminary findings of an investigation into the use of microwave, electric techniques and interdigitated (IDE) sensors functionalised with β -Bi₂O₃ based coatings for continuously detecting changes in the concentration of Zn in the range 0-10 mg/L in water.

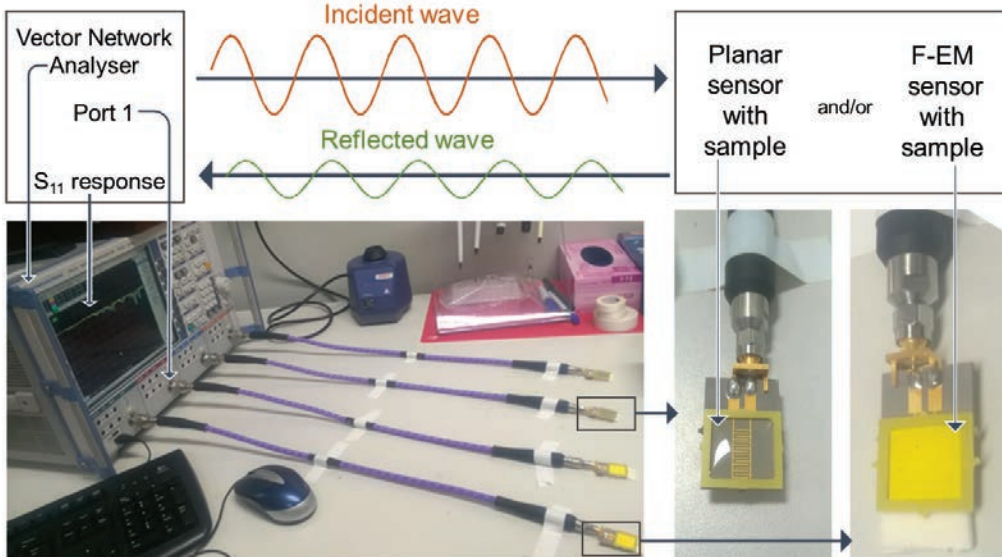


Figure 1 Scheme which explains the microwave interaction with a water sample placed on uncoated planar sensors and f-EM sensors: the incident waves, originated from a Vector Network Analyser (VNA), interact in a unique manner with the sample under test and generate a reflected signal (S_{11}) at specific EM frequencies.



Materials and methods

Microwave spectroscopy

The principle of microwave spectroscopy is based on the interaction between incident waves and the properties of the water sample presented to the sensing structure. This produces a reflected wave, with a spectral response at specific frequencies (Korostynska et al. 2013), as illustrated in fig. 1. The change in the reflection coefficient (S_{11}) can be linked to the composition and concentration of the measured solution, which depends on the variations in several parameters (such as conductivity, capacitance, resistance, and permittivity, as well as temperature, chemical structure, molecular composition, etc.). By specialising the sensor with some specific functional material (e.g. inorganic oxides, zeolites, organic polymers), it is possible to obtain a more specific signal, due to the physical or chemical interaction between the material and the analyte under test (Frau et al. 2017).

F-EM sensors

F-EM sensors are a novel alternative for improving the performance of the outgoing microwave spectroscopy and solve the lack of sensitivity and selectivity response for each metal, hence detecting lower concentrations than 1 mg/L and distinguishing between different metals. By combining functional materials and determining a consequent change in complex permittivity due to the singular interaction of the chemical material and the metal under test, it is possible to obtain a more specific EM spectrum response, with specific shifts in amplitude (in S_{11}) and/or in frequency (in Hz) at distinct frequencies.

Bismuth (Bi) has been used in the last two decades to detect Zn in water, mostly using electrochemical methods (Švancara et al. 2010). The nanoparticle form in particular has been shown to have superior sensing characteristics compared to the bulky Bi film electrode using electrochemical methods (Kadara et al. 2009). In addition, nanomaterials as inorganic oxide compositions are considered to be advantageous, owing to their strong adsorption (Sen Gupta and Bhattacharyya 2011).

In this work, planar Au eight-pair IDE sensors were functionalised with 60 μm of $\beta\text{-Bi}_2\text{O}_3$ based coatings as shown in fig. 2. $\beta\text{-Bi}_2\text{O}_3$ 90< Φ <210 nm particle size (Sigma-Aldrich 637017) (92.5 wt. %) was used as the principal chemical and was mixed with 7.5 wt. % of a binder (Butvar B98), and a suitable amount of ethylene glycol butyl ether (solvent). The paste mixture was printed with a semi-automatic screen-printer (Super Primex) for creating the thick film onto the planar sensors. Moreover, a set of Ag eight-pair IDE was screen-printed using a silver paste (Heraeus LCT3410) and functionalised with the same paste mixture based on $\beta\text{-Bi}_2\text{O}_3$ (fig. 3c, d).

The thickness of the thick film was increased by multiple screen-printing, with curing between each layer at 170°C. The final thickness (60 μm) was measured with a surface profiler (Taylor Hobson – Form Taly-surf 120).

Sample preparation

Water samples with various Zn concentrations (0, 0.1, 0.5, 1, 5, 10 mg/L) were prepared

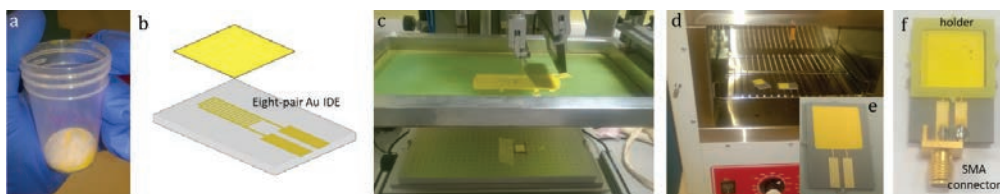


Figure 2 Manufacturing of the f-EM sensors: the mixture in powder form (a) was mixed with a binder and a solvent for reaching the right viscosity to be printed onto a planar sensor (b) using a screen-printer (c). The f-EM sensors were then put in an oven at 170°C (d); thus, the f-EM sensor (e) was welded with a SMA connector and a sample holder was settled onto it (f).



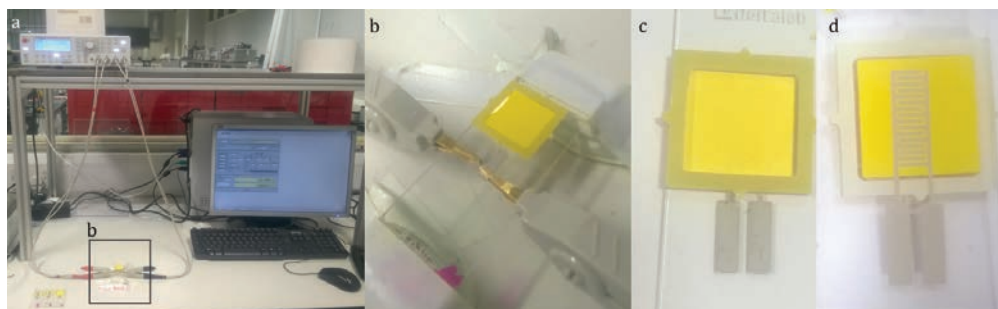


Figure 3 Set up of the impedance measurement using a LCR bridge connected to the screen-printed microscope slide with a Ag-IDE with $\beta\text{-Bi}_2\text{O}_3$ based coating (a-b); (c) front and (d) back of the functionalised Ag-IDE.

by spiking a precise volume of Zn 1,000 ppm ICP standard solution (Sigma-Aldrich 18562) in deionised water.

Experimental setup

In this experimental work, the microwave (reflected coefficient, S_{11} , dB) and electrical (capacitance, C_p , F, and resistance, R_p , Ω) properties were measured using f-EM sensors based on $\beta\text{-Bi}_2\text{O}_3$ and their interaction with the Zn samples at various concentrations:

- S_{11} was measured with a one-port configuration by connecting both uncoated and f-EM sensors to a Rohde and Schwarz ZVA 2.4 VNA through coaxial cables in the 100 MHz-8 GHz frequency range (as shown in fig. 1). For each measurement ($n=5$), 400 μL of Zn samples were allocated on the holder placed onto the sensor using a pipette;
- C_p and R_p were measured using a programmable LCR bridge HAMEG 8118 measured at low frequency (30 Hz-20 kHz) (fig. 3a): 400 μL of Zn samples

were placed on a coated Ag-IDE screen-printed on a microscope slide (fig. 3b, c, d) connected with the LCR bridge through a Rohde and Schwarz HZ184 Kelvin measurable cable.

Results and discussion

This work demonstrates the ability of this novel, electric and microwave sensing system combined with functional materials, to recognise and quantify Zn in water. Specifically, S_{11} measured with f-EM sensors with $\beta\text{-Bi}_2\text{O}_3$ based coating in the frequency range 1-4 GHz, as shown in fig. 4a, shows two pronounced amplitude shifts which are dependent on the Zn content. The peak at 1.57-1.68 GHz (magnified in fig. 4b) shows improved performance for detecting smaller changes in Zn concentrations, compared with the uncoated sensors (fig. 4c), where the concentration 0-1 mg/L of Zn are not separated (at 1.26 GHz).

This peak is set at a diverse frequency because there is an overall shift toward higher frequencies ($\Delta f_{\beta\text{-Bi}_2\text{O}_3 + \text{Zn samples}} = 300\text{-}400 \text{ MHz}$)

Table 2 Summary of statistical features obtained for electrical and microwave measurements of Zn water samples (0-10 mg/L).

Properties and sensing structure	Frequency	R^2	Sensitivity ^a	RSD (%)
C_p - coated IDE on microscope slide (60 μm)	150 Hz	0.998	0.79 nF	0.1 %
R_p - coated IDE on microscope slide (60 μm)	150 Hz	0.978 ^b	34 k Ω	2 %
S_{11} - uncoated EM sensor	1.26 GHz	0.983	0.0039 dB	0.9 %
S_{11} - f-EM sensor (60 μm)	1.57-1.68	0.960	0.0064 dB	1.5 %

^afor each 0.1 mg/L change of Zn concentration; ^blogarithmic correlation;



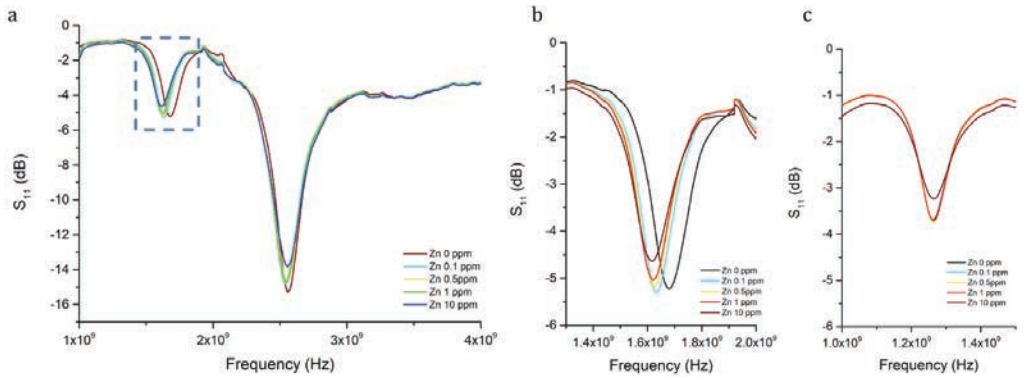


Figure 4 Microwave response for spiked-water with Zn at diverse concentrations at the frequency 1-4 GHz (a); the highlight area, where Zn concentrations < 1mg/L were better distinguished, is expanded in (b) and compared with the response obtained with the uncoated sensors (c) where the Zn content is not differentiated, demonstrating the increased performed produced by the f-EM sensor.

due to the thickness of the coating with a consequent change in dielectric properties (Patil and Puri 2010).

Overall results, obtained measuring Zn solutions at the range 0-10 mg/L using electrical and microwave techniques with coated and uncoated sensors are summarised in tab. 2, with R^2 , the sensitivity (as change of each parameter for 0.1 mg/L of Zn concentration) and RSD (relative standard deviation, as % of SD/mean). The signals were dependent on the type and concentration of Zn with $R^2 = 0.998$ and $R^2 = 0.978$, respectively for Cp and Rp (fig. 5a, b): Rp is related with Zn concentration and with the Cp with logarithmic correlation. Thereby, as the Cp and Zn con-

centration increase, the Rp decreases logarithmically.

Figures 5c and d show the linear correlations between Zn concentration and S_{11} , respectively $R^2 = 0.96$ and $R^2 = 0.98$ for the reflected coefficient measured with f-EM and uncoated sensors. Although the R^2 is slightly smaller with the f-EM sensor, it improves the capability of detecting changes of Zn especially at concentrations between 0-1 mg/L. Consequently, f-EM sensors were able to detect Zn concentrations in water with higher sensitivity than the uncoated sensors, especially to distinguish Zn concentrations both above and below the EQS established for surface water (0.1-0.2 mg/L).

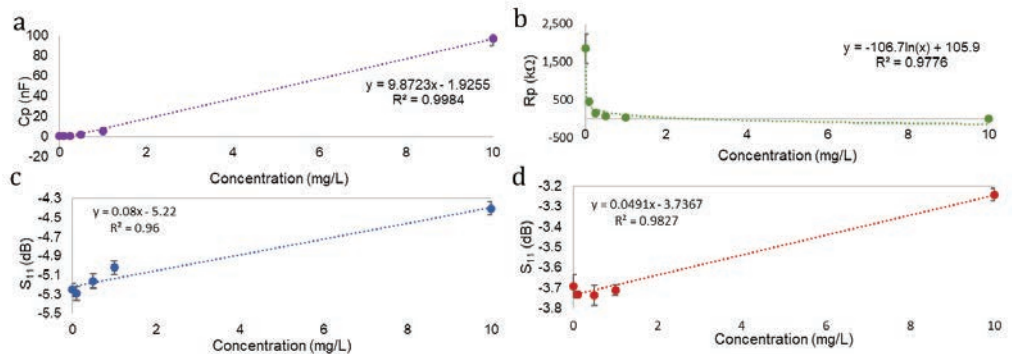


Figure 5 Correlation using functionalised Ag-IDE for Cp and Rp and Zn samples at 150 Hz, respectively linear (a) and logarithmic (b); Linear correlation between S_{11} coefficient and Zn samples (0-10 mg/L) using f-EM sensors (at 1.57-1.68) (c) and uncoated sensor (at 1.26 GHz) (d).



These effects are probably due to the effect of the permittivity variation of the sensitive chemical layer (Bernou et al. 2000). The overall propagation will depend on the permittivity of the substrate and its thickness, and on the sensitive material permittivity, which will change with the adsorption of the Zn ions in the sensitive layer. Whenever the Zn water samples were removed and the sensor was rinsed and allowed to dry, the sensor output returned to its baseline level (air spectra). This indicates that planar EM sensors are reusable, probably due to the weak solubility of metal oxides (Chu et al. 2017) and the reversible interaction between Zn and β -Bi₂O₃ based coating.

Conclusions

This work communicates the feasibility of using a novel EM sensing approach combined with f-EM sensors based on β -Bi₂O₃ for detecting Zn concentrations in water. Exposure of f-EM sensors to Zn-spiked-laboratory samples demonstrate the ability to detect continuous changes in Zn concentration with higher sensitivity than uncoated sensors, especially for concentrations in the range 0-1 mg/L. This level of sensitivity is significant as it enables the sensor to be used to monitor adherence to EQS. This method potentially offers a viable alternative to costly and labour intensive field sampling and laboratory-based methods of analysis.

Ongoing work is investigating new sensing materials to increase sensitivity and sensitivity for simultaneous analysis of multi-metal solutions and to move on the field to guarantee in situ and real-time monitoring.

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References

- Azmi A, Azman AA, Kaman KK, Ibrahim S, Mukhopadhyay SC, Nawawi SW, Yunus MAM (2017) Performance of Coating Materials on Planar Electromagnetic Sensing Array to Detect Water Contamination. *IEEE Sensors Journal* 17 (16):5244-5251. doi:10.1109/JSEN.2017.2720701
- Bernou C, Rebière D, Pistré J (2000) Microwave sensors: a new sensing principle. Application to humidity detection. *Sensors and Actuators B: Chemical* 68 (1):88-93. doi:10.1016/S0925-4005(00)00466-4
- Byrne P, Wood PJ, Reid I (2012) The Impairment of River Systems by Metal Mine Contamination: A Review Including Remediation Options. *Critical Reviews in Environmental Science and Technology* 42 (19):2017-2077. doi:10.1080/10643389.2011.574103
- Chu Z, Peng J, Jin W (2017) Advanced nanomaterial inks for screen-printed chemical sensors. *Sensors and Actuators B: Chemical* 243:919-926. doi:10.1016/j.snb.2016.12.022
- Cidu R, Frau F, Da Pelo S (2011) Drainage at Abandoned Mine Sites: Natural Attenuation of Contaminants in Different Seasons. *Mine Water and the Environment* 30 (2):113-126. doi:10.1007/s10230-011-0146-4
- Edokpayi J, Odiyo J, Popoola O, Msagati T (2016) Assessment of Trace Metals Contamination of Surface Water and Sediment: A Case Study of Mvudi River, South Africa. *Sustainability* 8 (2). doi:10.3390/su8020135
- Environment Agency (2008) Abandoned mines and the water environment. Science project SC030136.
- Frau I, Korostynska O, Byrne P, Mason A Continuous monitoring of Zn in water with bismuth oxide thick-film using microwave and electric techniques. In: 2017 Eleventh International Conference on Sensing Technology (ICST), 4-6 Dec. 2017. pp 1-6. doi:10.1109/IC-SensT.2017.8304479
- Kadara RO, Jenkinson N, Banks CE (2009) Disposable Bismuth Oxide Screen Printed Electrodes for the High Throughput Screening of Heavy Metals. *Electroanalysis* 21 (22):2410-2414. doi:10.1002/elan.200900266



- Kashin VK, Ivanov GM (2010) Zinc in natural waters in the Selenga River basin. *Water Resources* 37 (4):481-487. doi:10.1134/S009780781004007X
- Kashin VK, Ivanov GM (2010) Zinc in natural waters in the Selenga River basin. *Water Resources* 37 (4):481-487. doi:10.1134/S009780781004007X
- Korostynska O, Mason A, Al-Shamma'a AI (2013) Flexible microwave sensors for real-time analysis of water contaminants. *Journal of Electromagnetic Waves and Applications* 27 (16):2075-2089. doi:10.1080/09205071.2013.832393
- Korostynska O, Mason A, Al-Shamma'a AI (2013) Flexible microwave sensors for real-time analysis of water contaminants. *Journal of Electromagnetic Waves and Applications* 27 (16):2075-2089. doi:10.1080/09205071.2013.832393
- Patil S, Puri V (2010) Effect of bismuth oxide thick film overlay on microstrip patch antenna. *Microelectronics International* 27 (2):79-83. doi:10.1108/13565361011034759
- Patil S, Puri V (2010) Effect of bismuth oxide thick film overlay on microstrip patch antenna. *Microelectronics International* 27 (2):79-83. doi:10.1108/13565361011034759
- Sen Gupta S, Bhattacharyya KG (2011) Kinetics of adsorption of metal ions on inorganic materials: A review. *Advances in Colloid and Interface Science* 162 (1-2):39-58. doi:10.1016/j.cis.2010.12.004
- Sen Gupta S, Bhattacharyya KG (2011) Kinetics of adsorption of metal ions on inorganic materials: A review. *Advances in Colloid and Interface Science* 162 (1-2):39-58. doi:10.1016/j.cis.2010.12.004
- Švancara I, Prior C, Hočevar SB, Wang J (2010) A Decade with Bismuth-Based Electrodes in Electroanalysis. *Electroanalysis* 22 (13):1405-1420. doi:10.1002/elan.200970017
- Švancara I, Prior C, Hočevar SB, Wang J (2010) A Decade with Bismuth-Based Electrodes in Electroanalysis. *Electroanalysis* 22 (13):1405-1420. doi:10.1002/elan.200970017
- UK Technical Advisory Group on the Water Framework Directive (2008) UK environmental standards and conditions (phase 1 - SR1-2006).
- UK Technical Advisory Group on the Water Framework Directive (2008) UK environmental standards and conditions (phase 1 - SR1-2006).
- Wolkersdorfer C (2008) *Water Management at Abandoned Flooded Underground Mines — Fundamentals, Tracer Tests, Modelling, Water Treatment*. Springer, Heidelberg
- Wolkersdorfer C (2008) *Water Management at Abandoned Flooded Underground Mines — Fundamentals, Tracer Tests, Modelling, Water Treatment*. Springer, Heidelberg

